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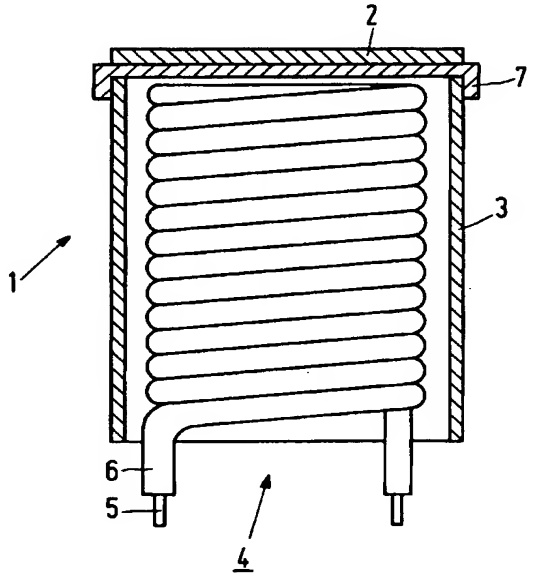
(54) Oxide cathode.

(57) The initial emission and the lifetime of oxide cathodes comprising, for example, BaO and SrO in their emissive layer are considerably improved by adding small quantities of rare earth metals (10-500 ppm).



EP 0 482 704 A1

The invention relates to a cathode having a supporting body substantially comprising nickel and being coated with a layer of electron-emissive material comprising alkaline earth metal oxides and comprising at least barium and a rare earth metal.

The invention also relates to a method of manufacturing such a cathode, and to an electron beam tube provided with a cathode according to the invention.

Such cathodes are described, for example, in EP-A-0,210,805. The emission of such cathodes is based on the release of barium from barium oxide. In addition to the barium oxide the electron-emissive material usually comprises strontium oxide and sometimes calcium oxide. Improved electron emission properties are obtained by the addition of rare earth metals. EP-A-0,210,805 teaches that the addition of rare earth metals should be at least 0.05% by weight to obtain at least some improvement of the emission.

The actual emission is mainly ensured by small areas (so-called "sites") having the lowest effective electron work function, which sites are spread over the electron-emissive material. In practice sites having a slightly higher work function will hardly contribute to the electron current generated by the cathode.

For a high effective electron emission it is therefore favourable to choose the number of sites having a minimal work function and the distribution of the sites over the emissive layer as optimally as possible.

It is one of the objects of the invention to realize such an optimum distribution in a cathode of the type mentioned in the opening paragraph with minimal additions of rare earth metals. It is another object of the invention to provide such a cathode which is well resistant to various manufacturing steps when it is being built into an electron tube, and which has a long lifetime.

A cathode according to the invention is therefore characterized in that the number of rare earth metal atoms in the electron-emissive material as a fraction of the number of alkaline earth metal atoms is 10-500 ppm and in that the rare earth metal atoms are distributed substantially uniformly over at least the upper part of the layer of emissive material.

In a preferred embodiment the layer of electron-emissive material is obtained by decomposition of a co-precipitated alkaline earth metal-rare earth metal compound.

In this respect it is to be noted that rare earth metals are not only understood to mean the metals of the lanthanides but also the metals yttrium and scandium. In this connection "distributed substantially uniformly" is understood to mean that each one of the separate particles of alkaline earth metal oxides in the layer of emissive material comprises rare earth metal atoms.

It is further to be noted that the provision of, for example, cerium in an emissive layer by means of co-precipitation is known *per se* from JP-A-74/12758. However, much larger quantities are concerned than in the present invention, viz. quantities within the range mentioned in EP-A-0,210,805.

A carbonate is preferably used for the alkaline earth metal-rare earth metal compound, but, for example, oxalates or formiates are alternatively possible.

The invention is based, *inter alia*, on the recognition that the uniform distribution of the rare earth metals leads to a uniform distribution of the number of sites. It is found that better cathode properties (higher emission, longer lifetime, etc.) are obtained when using smaller quantities of yttrium, seandium or one of the lanthanides than in cathodes without additions. Notably, additions of yttrium or europium yield good results.

Said lifetime improvement need not always become manifest in a reduced rate of the decrease of the emission, but may also become manifest in a less repid decrease of other properties which are important for the lifetime, such as, for example, the cut-off voltage. For example, a cathode according to the invention may have a decrease of the emission which is comparable to or even larger than that of a cathode in accordance with EP-A-0,210,805 with 2.5% by weight of Y_2O_3 in the emissive layer, but it may have further lifetime properties which are so much better that it is to be preferred for use in an electron tube. Moreover, said advantages of a better resistance to processing and use of fewer rare earth metals remain valid.

A method of manufacturing a cathode according to the invention is characterized in that a mixture of rare earth alkaline compounds is provided on the supporting body, in which the number of rare earth metal atoms as a fraction of the number of alkaline earth metal atoms is 10-500 ppm.

The invention will now be described in greater detail with reference to an embodiment and the drawing in which

Fig. 1 is a diagrammatic cross-sectional view of a cathode according to the invention.

The cathode 1 in Fig. 1 has a cylindrical nichrome cathode shaft 3 provided with a cap 7 in this embodiment. The cap 7 substantially comprises nickel and may comprise reducing means such as, for example, silicon, magnesium, manganese, aluminium and tungsten. The cathode shaft 3 accommodates a helical filament 4 which comprises a metal helically wound core 5 and an electrically insulating aluminium oxide layer 6.

An approximately 70 μm thick layer of emissive material 2 is present on the cap 7, which layer comprises, for example, a mixture of barium oxide, strontium oxide and a rare earth oxide obtained by providing and subsequently decomposing a co-precipitated barium strontium-rare earth carbonate, or a mixture of barium oxide, strontium oxide, calcium oxide and a rare earth oxide.

A carbonate comprising 60 ppm of yttrium (as a fraction of the number of alkaline earth metal atoms) was obtained by dissolving 20.1 kg of barium nitrate and 16.5 kg of strontium nitrate in 160 ml of water and by heating this mixture to 88 °C, together with 16.4 ml of an yttrium nitrate solution which comprised 50 mg of yttrium/litre. An aqueous solution comprising 18 kg of sodium carbonate was subsequently added thereto at a rate of 1.1 litre/minute so that a completely co-precipitated barium strontium yttrium carbonate was obtained. The carbonate thus obtained was subsequently filtered, washed and dried.

The desired suspension was obtained by adding 2 litres of a binder solution (diethyl carbonate to which a small quantity of binder material (cellulose nitrate) is added) to 1.1 kg of the co-precipitated carbonate.

Similarly, suspensions were prepared which comprised 300 ppm of europium.

Cathodes having an emissive layer of this type of carbonates comprising 60 ppm of yttrium atoms 300 ppm of europium atoms, respectively, (as a fraction of the alkaline earth metal atoms) were mounted in a cathode ray tube.

After this standard mounting and activation of the cathodes in the tube, with the carbonates decomposing to oxides, the cathode ray tubes were operated for 2000 hours at a filament voltage of 7 Volts, which is comparable with approximately 10,000 real operating hours. Before and after this life test emission measurements were performed at a filament voltage of 7 Volts after 30 seconds of conveying current at a cathode load of $2.2 A/cm^2$ (referred to as $\Delta i_{k,30}$ measurement).

The decrease in emission current was 2% when yttrium was added and approximately 5% when europium was added, while this decrease was 24% in the case without any additions. Moreover, the initial emission in all cases was found to be approximately 3% higher than in cathodes without any additions.

Also other properties such as, for example, the resistance to gases and a thermal treatment of the tube were found to be considerably better.

The above-mentioned values of Δi_k (decrease of emission current) are stated in Table I, as well as the decrease of the cut-off voltage (ΔV_k) and the slump (i.e. a measure of the emission current decrease). The Table also states the values for a cathode in accordance with EP-A-0,210,805 with 2.5% by weight of Y_2O_3 and for a cathode without additions.

TABLE I:

Type of addition	Δi_k	slump	ΔV_k
Addition 60 ppm of Y (distributed uniformly)	2%	1.3%	4.2%
Addition 300 ppm of Eu (distributed uniformly)	5%	2%	7.8%
2.5% by weight of Y_2O_3	4%	2%	5%
No addition	24%	6.2%	4.4%

It is apparent from the Table that in all respects the cathode with 60 ppm of Y atoms has better lifetime properties than the cathode with 2.5% by weight of Y_2O_3 and is by far better than a cathode without additions. Although the cathode with 300 ppm of Eu has a slightly poorer lifetime behaviour, it has all the advantages of a better resistance and less use of material (rare earth metals).

Similar lifetime tests as described hereinbefore were performed in other types of cathode ray tubes with cathodes in accordance with the invention in which 10 ppm of Eu, 60 ppm of Eu, 20 ppm of Y, 60 ppm of Y and 500 ppm of Y had been added to the emissive layer. The results are stated in Table II.

TABLE II:

Type of addition	Δi_k	slump	ΔV_k
10 ppm of Eu	13.6%	6.4%	2.5%
20 ppm of Y	10.4%	3.9%	1.6%
60 ppm of Eu	4.2%	2.6%	4%
60 ppm of Y	7.9%	1.9%	3.6%
500 ppm of Y	8.2%	4.6%	5.4%
No addition	30%	15%	3.2%

It is apparent from Table II that for small quantities (10-20 ppm) of rare earth metal atoms the emission decreases to a greater extent than in a cathode with 60 ppm of Y, but notably ΔV_k is much lower (under identical circumstances). Similar remarks as for the cathode with 300 ppm of Eu in Table 1 apply to the cathode with 500 ppm of Y.

In the latter series of tests one cathode was also tested which had an emissive layer consisting of a 40 µm thick layer without additions while on top of it a 20 µm thick layer was provided to which 60 ppm of Y atoms had been added in a uniformly distributed manner. The comparable values of Δi_k were 10%, 2% and 1.8%, respectively, so that also in this case notably the low decrease of the cut-off voltage leads to a long lifetime.

The invention is of course not limited to the embodiments shown, but several variations are possible. For example, the cathode may be designed in various manners (cylindrical, concave, convex, etc.) and there are various methods of providing the electron-emissive layer. This layer with the uniform distribution of the rare earth metals can also be obtained by depositing Ba-Sr-carbonade particles in a solution comprising yttrium (for example, an acetyl acetate) and by subsequent drying, with yttrium being left on each particle. By filtering, washing and drying an emissive material can then be obtained again with the powder thus obtained.

Claims

1. A cathode having a supporting body substantially comprising nickel and being coated with a layer of electron-emissive material comprising alkaline earth metal oxides and comprising at least barium and a rare earth metal, characterized in that the number of rare earth metal atoms in the electron-emissive material as a fraction of the number of alkaline earth metal atoms is 10-500 ppm and in that the rare earth metal atoms are distributed substantially uniformly over at least the upper part of the layer of emissive material.

2. A cathode as claimed in Claim 1, characterized in that the rare earth metal atoms are distributed substantially uniformly over the layer of emissive material.

3. A cathode as claimed in Claim 1 or 2, characterized in that the emissive layer is obtained by decomposition of a co-precipitated alkaline earth metal-rare earth metal compound.

4. A cathode as claimed in Claim 3, characterized in that the co-precipitated compound is a carbonate.

5. A cathode as claimed in Claim 1, 2, 3 or 4, characterized in that the layer of electron-emissive material comprises europium atoms or yttrium atoms.

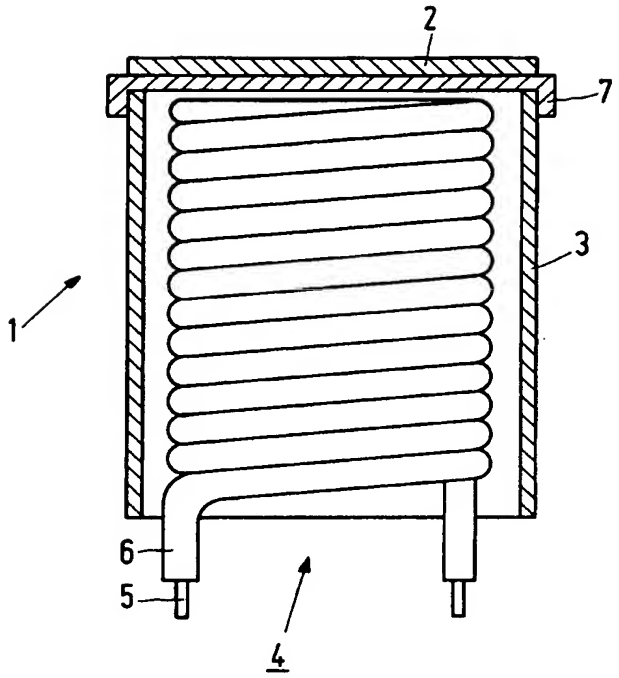
6. A cathode as claimed in Claim 1, 2, 3 or 4, characterized in that the electron-emissive material mainly comprises barium oxide and strontium oxide.

7. A cathode as claimed in any one of Claims 1 to 6, characterized in that the supporting body comprises reducing means.

8. An electron beam tube provided with a cathode as claimed in any one of Claims 1 to 7.

9. A method of manufacturing a cathode as claimed in any one of Claims 1 to 7, characterized in that an alkaline earth metal-rare earth metal compound is provided on the supporting body, in which compound the number of rare earth metal atoms as a fraction of the number of alkaline earth metal atoms is 10-500 ppm.

10. A method as claimed in Claim 9, characterized in that the compound comprises at least one co-precipitated alkaline earth metal-rare earth metal compound.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European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 91 20 2695

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
D,A	EP-A-0 210 805 (MITSUBISHI) * Abstract * * page 1, line 5 - page 1, line 25 * * page 4, line 10 - page 4, line 17 * * page 7, line 14 - page 8, line 7 * * page 21, line 3 - page 21, line 5 * * claims 1,2,22 * *	1,5-9	H 01 J 1/14 H 01 J 9/04
A	PATENT ABSTRACTS OF JAPAN vol. 13, no. 295 (E-783)(3643) 7 July 1989 & JP-A-01 076 638 (TOSHIBA) 22 March 1989 * abstract * *	1,3,4,10	
A	US-A-4 411 827 (D.M. CORNEILLE) * Abstract * * column 1, line 53 - line 62 * * claim 1 * *	1-3,9,10	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5) H 01 J

The present search report has been drawn up for all claims

Place of search	Date of completion of search	Examiner
The Hague	28 January 92	DAMAN M.A.

CATEGORY OF CITED DOCUMENTS

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